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"Comb-like Polymers Containing NLO Active Pendant groups"

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Comb-like polymers containing NLO active pendant groups

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SUMMARY:

The synthesis and characterization of new homo- and co-polymers containing p-extended (azomethine) active moiety separated by flexible methylene spacer have been reported. All the synthesized monomers and polymers showed spectroscopic properties (NMR, IR, UV) in accordance with the proposed structures. Inherent solubility of polymers in common organic solvents permits the measurement of the distribution of molecular weight from gel permeation chromatography. Thermal characteristics of the polymers are also described.

Introduction

There is a growing interest in organic materials as potential candidates for applications in nonlinear optical(NLO) devices¹⁻³). This is due to the large polarizabilities, which result from the complex excitation of delocalized p-electron system under appropriate electromagnetic fields as opposed to inorganic condensed-matter systems, of these materials.

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For the quadratic susceptibilities, $\chi^{(2)}$, an organic molecule must contain one or more acceptor and donor groups in appropriate positions to a π -delocalized moiety so that asymmetric charge-transfer occurs in the excited electronic state. In addition, the molecule itself should not possess any inversion symmetry and for macroscopic nonlinear effects a noncentrosymmetric molecular organization is necessary⁴⁻⁶). Factors such as planarity and conjugation length also contribute toward increasing the molecular hyperpolarizability⁷).

The design of an organic molecular and macromolecular systems based on aromatic Schiff's base consisting of suitably substituted electron donor and acceptor functional groups have been reported⁷⁻⁹). An organic molecule with this structural feature usually possesses facile intramolecular charge transfer, which in turn contributes significantly to its second order molecular hyperpolarizability, β .

Organic NLO materials, despite having large second order parameters, require convenient fabrication techniques for potential applications, since bulk crystals of these materials are not easy to grow or to handle. In recent years, the processing of NLO molecules has been improved to a great extent either by mixing homogeneously with suitable amorphous polymers¹⁰⁻¹⁴) or by attaching covalently to the polymers¹⁵⁻¹⁹).

One of the popular methods to obtain a noncentrosymmetric medium is through the application of strong electric field (commonly referred as poling)^{20,21}). A glassy polymer matrix (host)



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into which the NLO active material (guest) is homogeneously dispersed constitutes a simple system for poling studies. The macroscopic NLO susceptibility is proportional to $\mu\beta$ in such a system where β is the molecular hyperpolarizability and μ is the ground state dipole moment. A large ground state dipole moment leads to a higher degree of poling and molecular alignment forming a macroscopic noncentrosymmetric system. Limited solubility, active species migration and fast poling relaxation are some of the drawbacks encountered with such guest-host systems.

Comb-like side chain polymers consisting of covalently attached (to the flexible polymer backbone) NLO active pendant units are attractive alternative to guest-host systems. An advantage of using this system is that one can achieve higher densities, as high as 60 weight percent of nonlinear active groups and hence high nonlinear effects. Both the initial and long term decay in SH properties are reduced to a great extent.

In addition, it is possible to obtain side-chain liquid crystalline polymers if the backbone and the pendant group are disengaged by means of a spacer unit (consisting of a polymethylene sequence, for example). The pendant group in this case should be mesogenic besides being NLO active. Liquid crystalline organization can be preserved in the glassy state as well for these polymers and therefore it is expected that the poling-induced molecular orientation can be preserved for useful periods of time in such materials. In this work we have chosen a mesogen based on a donor or acceptor para-substituted Schiff's base. In addition to the facile synthesis of this strong mesogen the conjugated nature of this

moiety provides for easy charge transfer along the mesogen axis and allows for a purposeful introduction of an acceptor or donor group (such as CN or NO₂ here). The presence of the methyl group in the 2 position on the benzene ring is intended to lower the transition temperature by increasing the dihedral angle between the phenyl rings and broadening the mesogenic moiety. While such substitutions depress the T_c the effect is often not sufficient to produce a collapse of the mesophase. Moreover, the flexible spacer offers adequate flexibility to the side chains for the deposition of mono or multilayered films by the Langmuir-Blodgett(L-B) technique¹⁸).

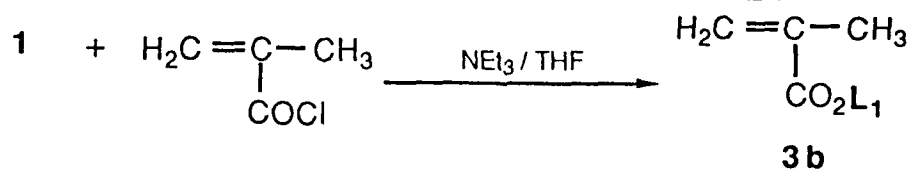
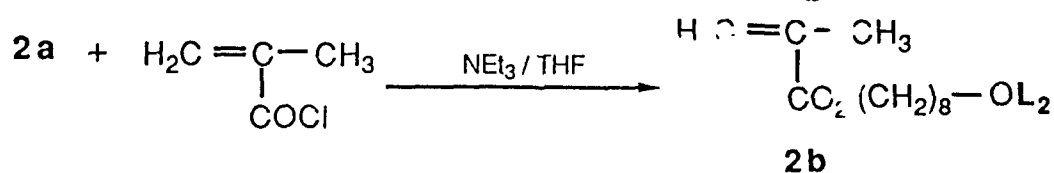
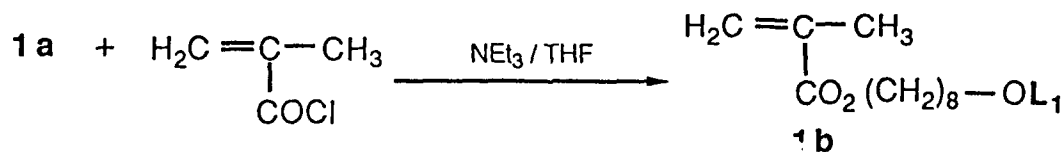
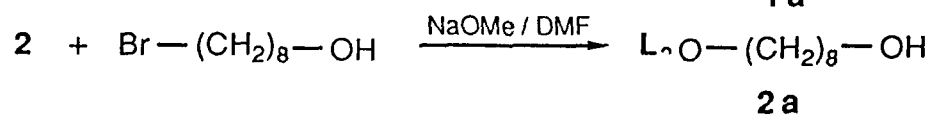
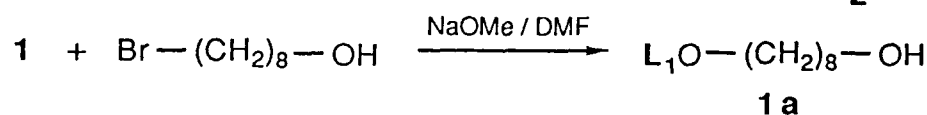
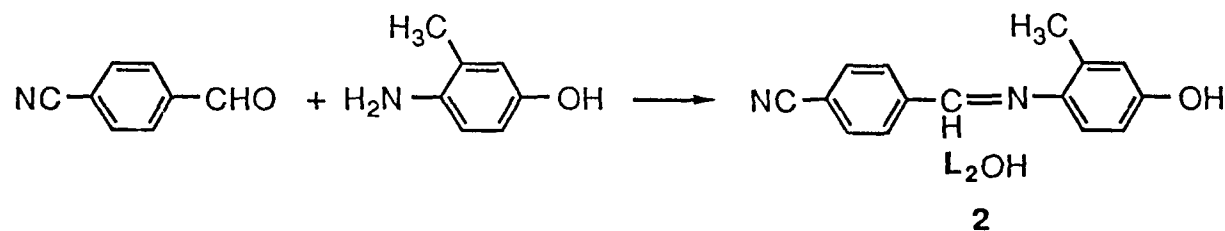
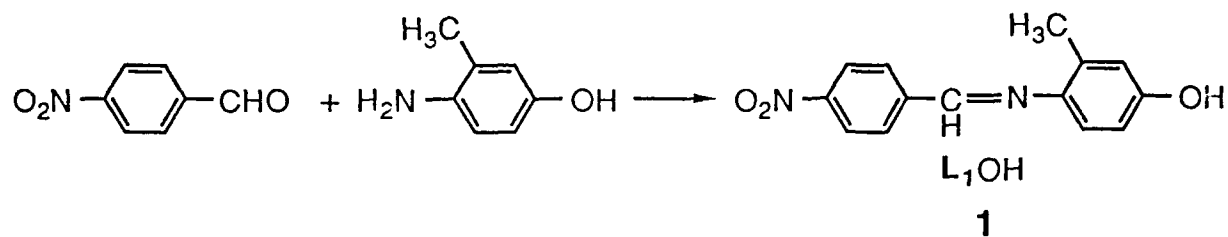
It is important to note that the structural requirements for a large optical nonlinearity may not be necessarily required for liquid crystallinity. Bearing this in mind, through a systematic study a number of compounds have been identified with the structure optimized for both possible mesomorphism and NLO properties⁸). We report here the synthesis and characterization of polymers and copolymers comprised of polymethylacrylate backbone and the Schiff's base units as mesogenic pendant groups. Thermal behavior of such polymers is also discussed.

Results and discussion

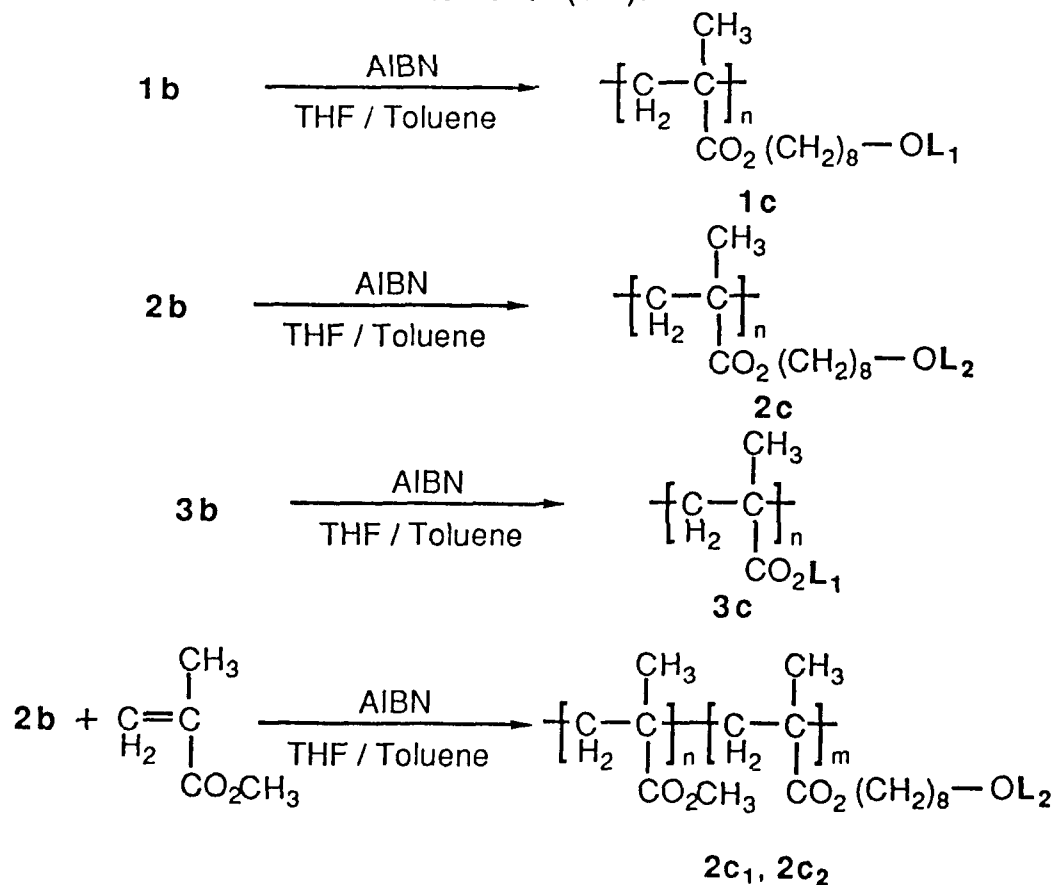
Polymer syntheses

The synthesis of polymerizable azo dye containing polymers has been reported in the literature¹⁵). Griffin and Vaidya²²) have

synthesized a number of liquid crystalline 1-alkanol derivatives containing unsymmetrical dimeric mesogen linked with azomethine group. A schematic representation for the synthesis of PMMA based polymers containing NLO active pendant groups is described below.



Azomethine compounds, 4-[4-Hydroxy 2-methylphenyl iminomethyl] nitrobenzene (**1**) and 4-[4-Hydroxy 2-methylphenyl iminomethyl] cyanobenzene (**2**), were synthesized by typical Schiff's base condensation reaction in the absence of catalyst²³). The water of condensation was removed from the reaction mixture by azeotropic distillation with benzene. O-alkylation of (**1**) and (**2**) was performed almost quantitatively by reacting their sodium salt with 8-bromo 1-octanol in dimethylformamide (DMF)²⁴). Esterification of **1a**, **2a** and **1** with methacryloyl chloride leads to NLO active monomers, 4-[4-(w-methacryloyloxy) octyloxy 2-methylphenyl iminomethyl] nitrobenzene (**1b**), 4-[4-(w-methacryloyloxy) octyloxy 2-methylphenyl iminomethyl] cyanobenzene (**2b**) and 4-[4-methacryloyloxy 2-methylphenyl iminomethyl] nitrobenzene (**3b**), respectively. Monomers **1b**, **2b** and **3b** were polymerized by free radical polymerization using AIBN as the radical initiator in THF/toluene (1:4).



Polymer properties

The physical properties of the polymers are listed in Tab. 1. The homopolymers (**1c** and **2c**) with flexible spacers in the side chains form low molecular weight product as observed from GPC measurement. While the homopolymer **3c** without flexible spacers produced reasonably high molecular weight product.

One of the difficulties associated with the use of organic chromophoric side groups (e.g., **3c**) relates to their deposition by L-B technique¹⁸). Too close packing of the chromophores (steric crowding) results in a rigid film which is undesirable as a degree of flexibility is required to enable the film to survive the stress it suffers during deposition.

In view of this two copolymers have been synthesized to increase the flexibility of the polymer backbone for the deposition of mono or multilayered films by L-B technique. High molecular weight product was obtained as the proportion of methylmethacrylate(MMA) is increased. Copolymers **2c₁** and **2c₂** were synthesized by copolymerization of MMA and **2b** using 5:1 and 18:1 ratios. Elemental analyses indicate that the ratio between the MMA and **2b** segments is 2.5 in **2c₁** and 9.5 in **2c₂**.

Tab. 1. Physical properties of homo and copolymers

Polymer	Molecular Weight ^{a)}			$T_g / ^\circ\text{C}$ ^{b)}	PDT / $^\circ\text{C}$ ^{c)}
	\overline{M}_w	\overline{M}_n	$\overline{M}_w / \overline{M}_n$		
1c	5000	1540	3,3	66	240
2c	4400	1670	2,6	52	285
2c₁	17700	3500	5,0	78	275
2c₂	86700	40500	2,1	89	266
3c	1181000	195000	6,1	-	350

^{a)} Molecular weight was determined by GPC. Measurements were done in THF using polystyrene standard as reference.

^{b)} T_g was determined by DSC.

^{c)} Product decomposition temperature(PDT) was determined from TGA curve.

Homo and copolymers having flexible spacers are essentially non crystalline in character (Tab. 1). Lower T_g values compared to PMMA ($T_g = 104^\circ\text{C}$) were observed in all cases due to the internal plasticizing effect arising from the flexible methylene group. Homopolymer **3c**, on the other hand, did not show any phase transition upto 175°C . The decomposition of **3c** in air was observed at 265°C . All polymers are thermally stable upto 240°C in nitrogen atmosphere as observed from the thermogravimetric analysis. Thermal stability of **3c** (350° vs. 240°C) is much higher because of lower aliphatic segments. Mesomorphic and nonlinear optical properties of these polymers will be published elsewhere.

Experimental part

Instrumentation. ^1H -NMR spectral data were obtained on a Bruker WP-270 NMR spectrometer. IR spectra were taken on a Bruker-IFS-113V FT-IR spectrophotometer. Ultraviolet-visible (UV-VIS) spectra were recorded on a Perkin-Elmer-559 spectrophotometer. Melting points were determined on a Thomas-Elnor capillary melting point apparatus and are uncorrected. Thermogravimetric measurements were carried out on a Perkin-Elmer-TGS-2 thermal analyzer under a flow of nitrogen (20 ml/min), with a heating rate of 20 K/min. The heats of phase transitions were determined with the aid of a Perkin-Elmer-2C differential scanning calorimeter under a flow of nitrogen, with heating rate 10 K/min.

Materials. 3-Methyl 4-nitrophenol (Aldrich) was purified by recrystallization from aqueous methanol. *p*-Nitrobenzaldehyde (Aldrich) and *p*-cyanobenzaldehyde (Aldrich) were used without further purification. DMF (Aldrich) was vacuum distilled from barium oxide before use. THF (Aldrich) and Toluene (Aldrich) were dried over sodium and distilled under nitrogen before use. 8-Bromo 1-octanol (Aldrich) was used as received. Methacryloyl chloride (Aldrich) was vacuum distilled under nitrogen prior to use. Methylmethacrylate(MMA) (Aldrich) was used as received. Solvent mixtures for chromatography were made up in volume/volume percentages. Analytical grade dichloromethane, toluene and

diethylether were stored over 4 Å molecular sieves and used for chromatographic separations. 2,2-Azoisobutyronitrile(AIBN) (Kodak) was crystallized from aqueous ethanol and stored in refreezarator.

Synthesis of the monomers

4-[4-Hydroxy 2-methylphenyliminomethyl] nitrobenzene (1): A modification of the method of Moffett²³⁾ was employed. A mixture of 200 mmol (30,22 g) 4-nitrobenzaldehyde and 200 mmol (24,63 g) 4-amino 3-methylphenol in benzene (600 ml) and ethanol (100 ml) was heated under nitrogen at 66°C. The water of condensation was removed by azeotropic distillation using a standard distillation set-up for 3 h. Evaporation of the solvent gave a solid which was purified by recrystallization twice from methanol in the form of orange needles. Yield: 42,15 g (82%); m.p. 135°C.

IR(KBr): 1518, 1342 (s; NO₂), 1626 (s; N=CH), 3343 cm⁻¹ (w; O-H).

UV-VIS(CHCl₃): λ/nm = 268, 390 (λ_{max}), 510 (cut off).

C ₁₄ H ₁₂ O ₃ N ₂ (256)	Calc.	C	65,56	H	4,72	N	10,93
	Found	C	64,04	H	5,22	N	10,34

4-[4-Hydroxy 2-methylphenyliminomethyl] cyanobenzene (2): Following the same procedure as described for the preparation of **1** starting from 200 mmol (26,22 g) 4-cyanobenzaldehyde and 200 mmol (24,63 g) 4-amino 3-methylphenol the title compound was obtained as yellow needles. Yield: 35,64 g (75%); m.p. 190°C.

IR(KBr): 2237 (s; C≡N), 1626 (s; N=CH), 3368 cm⁻¹ (w; O-H).

UV-VIS(CHCl₃): λ/nm = 252, 365 (λ_{max}), 455 (cut off).

C ₁₅ H ₁₂ ON ₂ (236)	Calc.	C	76,25	H	5,12	N	11,86
	Found	C	75,83	H	5,10	N	11,70

4-[4-(w-Hydroxy) octyloxy 2-methylphenyliminomethyl] nitrobenzene (1a): To a solution of 19,53 mmol (1,05 g) NaOMe in 100 ml methanol 19,53 mmol (5.0 g) **1** was added and stirred for 10 min. After the addition of 10 ml of dry toluene the solvents were evaporated to dryness under reduced pressure. The solid residue was cooled to room temperature and 19,52 mmol (4,08 g) 8-bromo 1-octanol in 25 ml of freshly distilled DMF was added. The resulting mixture was stirred for 2 h at 110°C under nitrogen. The brown solution was then cooled and poured into 250 ml cold water. The product was extracted with diethylether and dried (MgSO₄). Evaporation of the solvent gave an oil which was purified by column chromatography (silica gel, dichloromethane/diethylether 1:1 as eluent) yielding a liquid which solidified on cooling to an orange red solid. Yield: 6,75 g (90%); m.p. 60°C.

IR(KBr): 1240 (s; C-O-C), 1624 (s; N=CH), 1516, 1339 (s; NO₂), 3439 cm⁻¹ (w; O-H).

UV-VIS(CHCl₃): λ /nm = 268, 390 (λ_{max}), 500 (cut off).

C ₂₂ H ₂₈ O ₄ N ₂ (384)	Calc.	C	68,73	H	7,34	N	7,29
	Found	C	68,48	H	7,37	N	7,20

4-[4-(w-Hydroxy) octyloxy 2-methylphenyliminomethyl] cyanobenzene (2a): Following the same procedure as described for the preparation of **1a** starting from 106,50 mmol (25,16 g) **2**, 106,50 mmol (5,75 g) NaOMe and 106,50 mmol (22,27 g) 8-bromo 1-octanol the title compound was obtained as a yellow solid when the reaction mixture poured into ice water. Yield: 36,87 g (95%); m.p. 71°C.

IR(KBr): 2228 (s; C≡N), 1236 (s; C-O-C), 1620 (s; N=CH), 3534 cm⁻¹ (w; O-H).

UV-VIS(CHCl₃): λ /nm = 255, 365 (λ_{max}), 465 (cut off).

C ₂₃ H ₂₈ O ₂ N ₂ (364)	Calc.	C	75,79	H	7,74	N	7,69
	Found	C	75,75	H	7,60	N	7,64

4-[4-(w-methacryloyloxy) octyloxy 2-methylphenyl iminomethyl] nitrobenzene (1b): 19,68 mmol (2,06 g) methacryloyl chloride was added dropwise to a solution of 16,40 mmol (6,30 g) **1a** and 24,60 mmol (2,49 g) triethylamine in THF (40 ml) and stirred for 12 h at room temperature. After being refluxed for further 2 h under nitrogen the solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, dichloromethane/diethylether 60:40 as eluent) as an orange-red liquid. Yield: 7,10 g (95%).

IR(neat): 1717 (s; CO₂), 1522, 1344 (s; NO₂), 1626 (s; N=CH), 1240 cm⁻¹ (s; C-O-C)

UV-VIS(CHCl₃): λ/nm = 268, 390 (λ_{max}), 500 (cut off).

C ₂₆ H ₃₂ O ₅ N ₂ (452)	Calc.	C	69,00	H	7,13	N	6,19
	Found	C	68,90	H	6,95	N	5,99

4-[4-(w-methacryloyloxy) octyloxy 2-methylphenyl iminomethyl] cyanobenzene (2b): Following the same procedure as described for the preparation of **1b** starting from 55,50 mmol (20,25 g) **2a**, 66,6 mmol (6,93 g) methacryloyl chloride and 77,70 mmol (7,86 g) triethylamine the title compound was obtained as a yellow solid. Yield: 22,32 g (93%); m.p. 55°C.

IR(KBr): 1713 (s; CO₂), 2224 (s; C≡N), 1626 (s; N=CH), 1238 cm⁻¹ (s; C-O-C).

UV-VIS(CHCl_3): $\lambda/\text{nm} = 255, 365 (\lambda_{\text{max}}), 465$ (cut off).

$^1\text{H-NMR}(\text{CDCl}_3)$: $\delta = 1,04\text{-}2,17(\text{m}, 12\text{H}, \text{aliphatic CH}_2 ; 3\text{H}, \text{aliphatic C-CH}_3)$; $2,40(\text{s}, 3\text{H}, \text{Ar-CH}_3)$; $3,97(\text{t}, 2\text{H}, \text{Ar-O-CH}_2)$; $4,13(\text{t}, 2\text{H}, \text{O-CH}_2)$; $6,60\text{-}8,09(\text{m}, 7\text{H}, \text{ArH})$; $8,45(\text{s}, \text{H}, \text{N=CH})$.

$\text{C}_{27}\text{H}_{32}\text{O}_3\text{N}_2(432)$	Calc.	C	74,97	H	7,46	N	6,48
	Found	C	74,50	H	7,43	N	6,29

4-[4-methacryloyloxy 2-methylphenyl iminomethyl] nitrobenzene (**3b**): Following the same procedure as described for the preparation of **1b** starting from 17,20 mmol (4,40 g) **1**, 19,0 mmol (1,99 g) methacryloyl chloride and 19,0 mmol (1,92 g) triethylamine the title compound was obtained as yellow needles after crystallization from acetone. Yield: 2,79 g (50%); m.p. 143°C .

IR(KBr): $1734 (\text{s}; \text{CO}_2)$, $1632 \text{ cm}^{-1} (\text{s}; \text{N=CH})$.

$\text{C}_{18}\text{H}_{16}\text{O}_4\text{N}_2(324)$	Calc.	C	66,65	H	4,97	N	8,64
	Found	C	66,65	H	5,03	N	8,56

Synthesis of the polymers

Polymer 1c: 15,47 mmol (7,0 g) **1b** in 65 ml of THF/toluene(1:4) mixture was allowed to react with 0,31 mmol (0,05 g) AIBN under nitrogen for 72 h at 70°C . The dark brown solution was then

precipitated into methanol. The product was purified by reprecipitation from DMF with methanol giving an orange solid. Yield: 4,1 g (57%).

IR(KBr): 1726 (s; CO₂), 1626 (s; N=CH), 1522, 1342 (s; NO₂), 1242 cm⁻¹ (s; C-O-C).

UV-VIS(CHCl₃): λ /nm = 267, 385 (λ_{\max}), 503 (cut off).

(C ₂₆ H ₃₂ O ₅ N ₂) _n (452) _n	Calc.	C	69,00	H	7,13	N	6,19
	Found:	C	68,96	H	7,27	N	6,08

Polymer 2c: Following the same procedure as described for the preparation of polymer **1c** starting from 23,12 mmol (10,0 g) **2b** and 0,61 mmol (0,10 g) AIBN the title compound was obtained as a yellow solid. Yield: 6 g (60%).

IR(KBr): 2228 (s; C≡N), 1726 (s; CO₂), 1242 (s; C-O-C), 1626 cm⁻¹ (s; N=CH).

UV-VIS(CHCl₃): λ /nm = 255, 365 (λ_{\max}), 465 (cut off).

¹H-NMR(CDCl₃): δ = 0,54-2,55(m, 12H, aliphatic CH₂ ; 3H, aliphatic C-CH₃, 3H, Ar-CH₃); 3,50-4,25(b, 2H, Ar-O-CH₂, 2H, O-CH₂); 6,46-8,06(m, 7H, ArH); 8,38(s, H, N=CH).

(C ₂₇ H ₃₂ O ₃ N ₂) _n (432) _n	Calc.	C	74,97	H	7,46	N	6,48
	Found	C	73,55	H	7,42	N	6,00

Polymer 3c: Following the same procedure as described for the preparation of polymer **1c** starting from 1,65 mmol (0,60 g) **3b** and 0,012 mmol (0,002 g) AIBN the title compound was obtained as a yellow solid. Yield: 0,24 g (40%).

IR(KBr): 1748 (s; CO₂), 1628 cm⁻¹ (s; CH=N).

(C ₁₈ H ₁₆ O ₄ N ₂) _n (324) _n	Calc.	C	66,65	H	4,97	N	8,64
	Found	C	66,65	H	5,02	N	8,55

Polymer 2c₁: 24,35 mmol (2,44 g) MMA and 0,12 mmol (0,02 g) AIBN in 25 ml of THF were added to a solution of 4,87 mmol (2,11 g) **2b** and 0,06 mmol (0,01 g) AIBN in 2 ml of THF/toluene(1:5) mixture after every 7 h for 7 times and stirred under nitrogen at 80°C. After being stirred for another 24 h followed by the work-up described for polymer **1c** the title compound was obtained as a light yellow solid. Yield: 2,5 g (55%).

IR(KBr): 2227 (s; C≡N), 1729 (s; CO₂), 1624 (s; N=CH), 1241 cm⁻¹ (s; C-O-C).

UV-VIS(CHCl₃): λ/nm = 255, 365 (λ_{max}), 465 (cut off).

¹H-NMR(CDCl₃): δ = 0,90-1,92(m, aliphatic CH₂; aliphatic C-CH₃); 2,38(s, Ar-CH₃); 3,62(t, Ar-O-CH₂); 3,99(t, O-CH₂); 6,55-8,09(m, ArH); 8,42(s, N=CH).

Anal.	Found	C	68,97	H	7,43	N	4,06
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Polymer 2c₂: 87,66 mmol (8,78 g) MMA and 0,12 mmol (0,02 g) AIBN in 50 ml of THF were added to a solution of 4,87 mmol (2,11 g) **2b** and 0,09 mmol (0,015 g) AIBN in 2 ml of THF/toluene(1:5) mixture after every 7 h for 7 times and stirred under nitrogen at 80°C. After being stirred for another 24 h followed by the work-up described for polymer **1c** the title compound was obtained as a light yellow solid. Yield: 6,5 g (60%).

IR(KBr): 2227 (s; C≡N), 1729 (s; CO₂), 1624 (s; N=CH), 1242 cm⁻¹ (s; C-O-C).

¹H-NMR(CDCl₃): δ = 0,50-2,08(m, aliphatic CH₂; aliphatic C-CH₃); 2,36(s, Ar-CH₃); 3,55(b, Ar-O-CH₂); 3,90(b, O-CH₂); 6,58-8,09(m, ArH); 8,44(s, N=CH).

Anal.	Found	C	63,33	H	7,92	N	2,06
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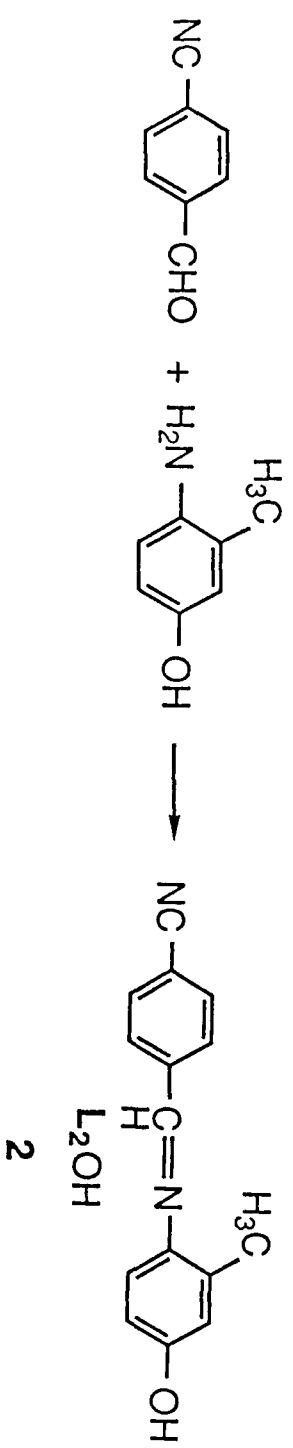
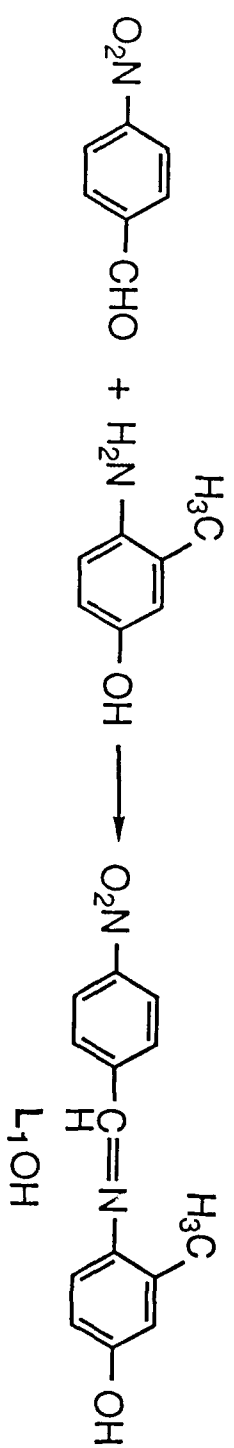
Acknowledgment

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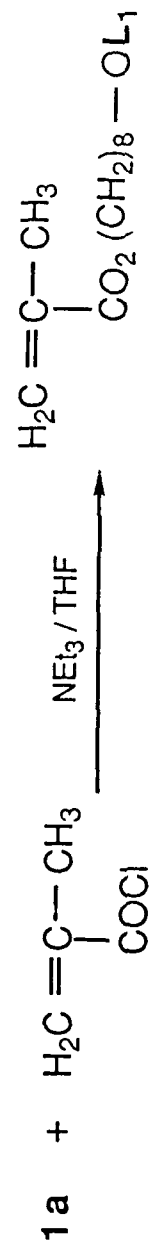




1a



2a



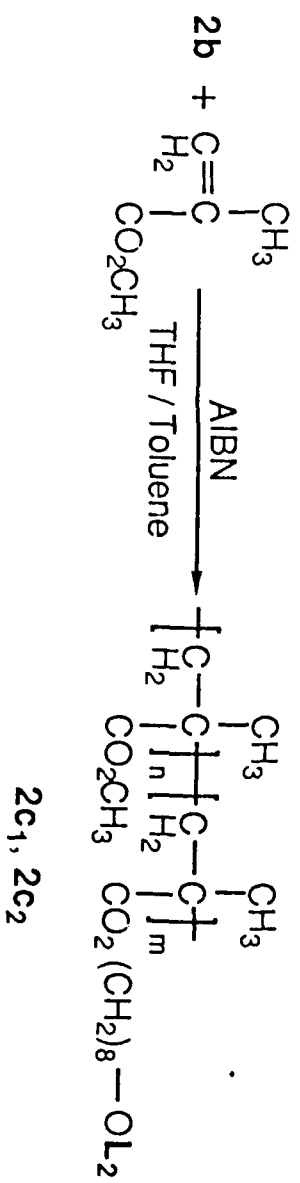
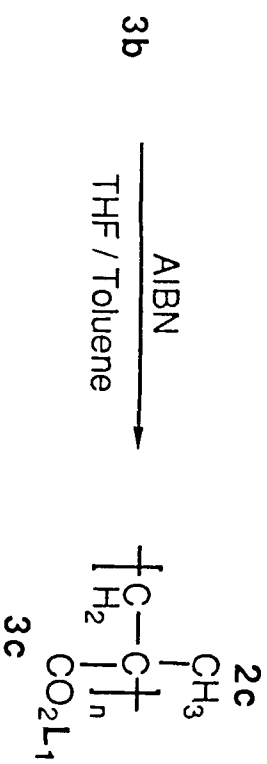
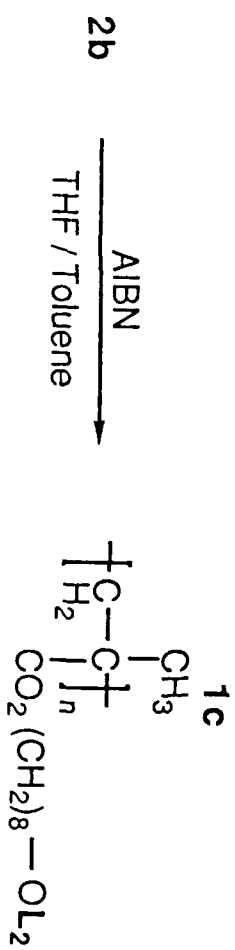
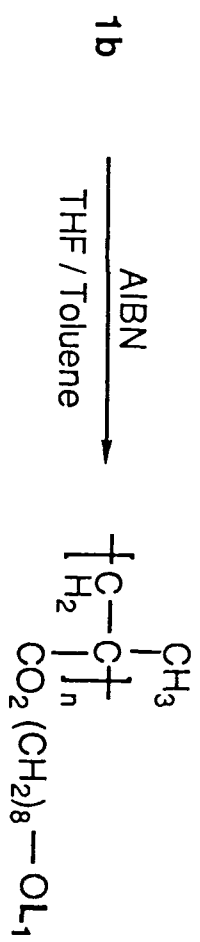
1b



2b



3b



Tab. 1. Physical properties of homo and copolymers

Polymer	Molecular Weight ^{a)}		$T_g / ^\circ\text{C}$ ^{b)}	PDT / $^\circ\text{C}$ ^{c)}
	\overline{M}_w	\overline{M}_n $\overline{M}_w / \overline{M}_n$		
1c	5000	1540 3,3	66	240
2c	4400	1670 2,6	52	285
2c ₁	17700	3500 5,0	78	275
2c ₂	86700	40500 2,1	89	266
3c	1181000	195000 6,1	-	350

^{a)} Molecular weight was determined by GPC. Measurements were done in THF using polystyrene standard as reference.

^{b)} T_g was determined by DSC.

^{c)} Product decomposition temperature(PDT) was determined from TGA curve.